CHAPTER 3

RESULTS AND DISCUSSION

NAPHTHALENE LUMINOPHORS
Fluorescence studies of naphthalene luminophors:

The preparation of multicomponent luminophors needs the knowledge of photophysical behaviour of individual components. Hence, with a view to understand photophysics of emission, the absorption, excitation and fluorescence spectra of the organic compounds of interest are discussed in the first stage. These studies helped in selecting the materials as host and guest for preparation of bicomponent and tricomponent organo-luminophors.

3.1 Absorption, excitation and fluorescence studies of naphthalene:

Fig. 3.1 shows the absorption, excitation and fluorescence spectra of crystalline naphthalene. The absorption spectrum of the naphthalene presented in the figure is structured having the bands at 362, 381, 392 nm. The spectrum does not consists a solution type Frank-condon envelop. This is due to the molecular packing in the crystalline material. The naphthalene belongs to a lattice A type, which involves a very small orbital overlap between the \( \pi \) molecular orbitals of the adjacent molecules. The fluorescence spectrum of naphthalene is structured and shows the emission peaks at 341, 390, 412 and 435 nm. The absorption and emission spectrum are mirrored and shows negligible Stokes shift. The emission is appeared in
Fig. 3.1 Absorption (a), Fluorescence (b), and Excitation (c) spectrum of pure naphthalene.
the violet sector of the visible spectrum, hence upon excitation, the naphthalene will be excited to its singlet excited electronic state which results in the formation of naphthalene exciton. From the better overlap between absorption and emission spectrum, it is concluded that the emission should originate from the lowest energy free exciton level of the molecule. If in such molecule an impurity is present then the excitation energy of the exciton should be trapped by an impurity. The electronic excitation energy transfer (EET) process would result in changing the emission behaviour of naphthalene. The naphthalene crystal can be used as a host and its emission properties can be changed, by doping it intentionally with highly fluorescent materials having emission regions towards longer wavelength side.

3.2 Bicomponent naphthalene luminophors:

The fluorescent impurities such as anthracene, pyrene, perylene and phenanthrene were tested. Fig. 3.2 shows absorption spectra of above fluorescent compounds and the emission spectrum of the naphthalene. The sufficient overlap between absorption and emission spectrum indicates an efficient transfer of excitation energy from naphthalene exciton to anthracene as well as to pyrene, which may change the naphthalene emission spectrum. In contrast, the absorption
Fig. 3-2
Overlap between emission spectrum (---) of naphthalene and absorption spectra (....):
a. anthracene,  
b. pyrene,  
c. phenanthrene, and  
d. perylene.
spectrum of perylene is separate from the naphthalene emission spectrum and has negligible overlap. Similarly, the phenanthrene absorption spectrum has poor overlap. Therefore, transfer of excitation energy from naphthalene to phenanthrene and to perylene is inefficient. From these results, it was planned to prepare bicomponent systems of naphthalene using pyrene and anthracene.

**Bicomponent systems:**

**3.2.1 Anthracene doped naphthalene:**

**3.2.2 Pyrene doped naphthalene:**

Fig.3.3 represents fluorescence spectra of pure naphthalene (a), naphthalene doped by anthracene (b), and naphthalene doped by pyrene (c). The naphthalene fluorescence is quenched by both anthracene and pyrene. The emission spectrum of anthracene doped naphthalene is structured with maximum emission at 421 nm. The emission corresponds to the fluorescence spectrum of crystalline anthracene. The intensity of emission band increases with increase in concentration of anthracene from $10^{-3}$ to $10^{-2}$ mole. The fluorescence spectrum of pyrene doped naphthalene(c) is broad, structureless having $\lambda_{\text{max}} = 474$ nm and is similar to the excimer emission first observed by Förster and Kasper. In the spectra of doped naphthalene, the fluorescence emission band of naphthalene
Fig. 3.3
a. Fluorescence spectrum of Pure Naphthalene
b. Fluorescence spectra of Anthracene doped Naphthalene
c. Fluorescence spectra of Pyrene doped Naphthalene and pure Pyrene.
expected to occur in the region 325-425 nm are not observed. This observation indicates that the naphthalene excitons generated by absorption of energy migrate over the sufficient distance where its energy is trapped by impurity molecule in the naphthalene lattice.

The anthracene and pyrene occupy the lattice sites in naphthalene, when mixed crystals of naphthalene melt containing anthracene or pyrene was grown. The electronic EET from naphthalene to anthracene and to pyrene is possible only in the mixed crystals as the distance over which the naphthalene exciton migrates is of the order of molecular diameter. The proposed mechanism of exciton migration in host-guest system can be confirmed by recording the fluorescence spectra of some host-guest pair in solution. Fig. 3.4 shows fluorescence spectra of solution of anthracene doped naphthalene and pyrene doped naphthalene in benzene. These fluorescence spectra of solution systems shows emission bands corresponding to individual components with disappearance of some of the initial bands may be due to re-absorption of excitation energy. These experiments indicate that the exciton energy transfer is probable only in doped crystalline materials and is absent in solution where distance between the two neighbouring molecule is large.
Fig. 3.4 Fluorescence spectra of pyrene doped naphthalene (a) and anthracene doped naphthalene (b) in benzene
The pyrene doped naphthalene emits bluish green colour and it is interesting to note that intensity of doped naphthalene is greater than that of the excimer fluorescence of bare crystalline pyrene. The excimer emission of crystalline pyrene is also shown in Fig. 3.3 (c) for sake of comparison.

**Bicomponent systems for selection of second guest:**

3.2.3 Phenanthrene doped naphthalene:

3.2.4 Perylene doped naphthalene:

The pyrene and anthracene were used as first guest, in naphthalene host. During preparation of multicomponent naphthalene luminophors, the second guest component having interaction either with host or first guest must be used. Fluorescent perylene and phenanthrene were tested as guests in the naphthalene.

Fig. 3.5 shows fluorescence spectra of phenanthrene doped naphthalene and perylene doped naphthalene along with the fluorescence spectra of pure naphthalene. The spectrum of phenanthrene doped naphthalene shows the intense bands at about 410 nm and weak band at about 420 nm and corresponds with the last two bands of the emission spectrum of pure naphthalene. The excitation energy of naphthalene corresponding to the first two bands at 345 and 395 nm might be absorbed by phenanthrene. The bands corresponding to
Fig. 3.5
Fluorescence spectra:
a. Pure Naphthalene,  
b. Phenanthrene doped naphthalene and  
c. Perylene doped naphthalene.

Fig. 3.6
Fluorescence Spectrum of pure pyrene (a), and absorption spectrum of pure  
perylene (b).
phenanthrene are not observed in doped naphthalene. The fluorescence spectrum of perylene doped naphthalene is weak and corresponds to the naphthalene fluorescence. The excimer and monomer emission of perylene impurity is not seen in the spectrum. These observations led to conclude that the phenanthrene and perylene impurities, quenches the fluorescence of naphthalene. Therefore, these fluorescent compounds can not be used as guests to prepare multicomponent naphthalene luminophors.

However, perylene has energetic interactions with pyrene and anthracene, hence it can be used as second guest in naphthalene system. In addition to that the absorption spectrum of perylene has a good overlap with the emission spectrum of pyrene as is shown in Fig.3.6. Because of the overlap, the emitted energy of pyrene can be trapped by perylene molecule before it emits. Phenanthrene does not have interaction with pyrene and anthracene, because of which it was not used during preparation of naphthalene multicomponent systems.

Energy level diagram:

Fig. 3.7 represents energy level diagram of naphthalene, pyrene and perylene. Figure shows first excited singlet and triplet exciton energy levels of the individual components. The
diagram is constructed by using the available information.\textsuperscript{80,111} The singlet and triplet energy levels of perylene lie below the corresponding energy levels of pyrene indicating the possibility of EET from pyrene to perylene. Similarly, the lattice structure of pyrene and perylene are known to favor the formation of exciplex due to lateral overlapping of π*-molecular orbitals.\textsuperscript{112} The exciplex is characterized by its emission appearing towards red. Hence to take advantage of this fact the pyrene (G1) and perylene (G2) were used as two guests to prepare multicomponent naphthalene luminophors.

3.3 Tricomponent naphthalene luminophors: pyrene and perylene doped naphthalene:

Fig. 3.8 presents fluorescence spectra of pure naphthalene, pyrene doped naphthalene and pyrene and perylene doped naphthalene. It is observed that the addition of perylene as a second impurity shifts the fluorescence spectrum of pyrene doped naphthalene. The broad excimer emission of pyrene is completely quenched and a new broad emission band centered at wavelength

\[ \lambda_{\text{max}} = 483 \text{ nm} \]

appeared at concentration $10^{-3}$ mole perylene per mole naphthalene. Some of the emission bands of naphthalene are also observed in the blue region. The broad emission band is attributed to the CT state formed due to interactions of pyrene
Fig. 3.7 Energy level diagram of naphthalene, pyrene, and perylene.

Fig. 3.8
Fluorescence spectra:
a. Pure Naphthalene,  b. Pyrene doped Naphthalene and
c. Pyrene and Perylene doped Naphthalene.
and perylene. When the pyrene and perylene containing naphthalene crystals were grown from the melt, the pyrene and perylene molecules replace the naphthalene host molecules by closely fitting into the empty lattice sites. This double replacement forms naphthalene lattice containing pyrene and perylene guests. The stack sequences is of the type DG1G2DG1G2D--- and is known as mixed stacks. The fluorescence spectrum of this mixed naphthalene presented in Fig.3.8 does not show the emission of individual components. From this observation it is concluded that the introduction of pyrene and perylene form homogeneous solid solution in naphthalene.

The above experiments indicate that the presence of perylene in the naphthalene ternary systems serves as wavelength shifter. By varying the concentration of perylene in naphthalene doped binary system, the naphthalene ternary luminophors were prepared. The composition and optical characteristics of naphthalene ternary luminophors are given in Table no. 2.1 and graphically presented in Fig. 3.9, 3.10 and 3.11.

Fluorescence spectra of naphthalene containing $10^{-3}$ mole pyrene and varying amounts of perylene are shown in Fig. 3.9. At lower concentrations of the impurity, the figure shows, initial
Fig. 3.9
Fluorescence spectra of naphthalene containing $10^{-3}$ mole pyrene and varying amounts of perylene.

a. $10^{-3}$ mole perylene  b. $10^{-2}$ mole perylene  c. $10^{-1}$ mole perylene
Fig. 3.10
Fluorescence spectra of naphthalene containing $10^{-2}$ mole pyrene and varying amounts of perylene.

- a. $10^{-3}$ mole perylene
- b. $10^{-2}$ mole perylene
- c. $10^{-1}$ mole perylene
Fig. 3.11
Fluorescence spectra of naphthalene containing $10^{-1}$ mole pyrene and varying amounts of perylene.

a. $10^{-3}$ mole perylene  

b. $10^{-2}$ mole perylene  

c. $10^{-1}$ mole perylene
emission bands in short wave region which corresponds to the longer wavelength emission bands of naphthalene. However, at higher concentrations these bands are quenched. At concentration of $10^{-3}$ mole perylene in pyrene doped naphthalene, the spectrum shows a broad structureless emission band peaking at 484 nm, in addition to long wavelength emission bands of naphthalene. The observed structureless emission band does not correspond either with the exciplex emission band of pyrene- perylene crystalline luminophor or with the excimer emission of crystalline pyrene. As the concentration of perylene increases the long wavelength emission bands of naphthalene are quenched with simultaneous shift of the structureless band towards red. Hence, at a concentration $10^{-2}$ mole perylene the weak structureless band is appeared in the region 490-575 nm. However, at concentration $10^{-1}$ mole perylene, the naphthalene emission is completely quenched and a single structureless band appears with a maximum emission at 612 nm.

Fig. 3.10 represents the fluorescence spectra of ternary naphthalene containing $10^{-2}$ mole pyrene and varying amounts of perylene. As compared to the spectra shown in earlier figure, the fluorescence of these luminophors show very weak longer wavelength emission bands of naphthalene. It is seen that the
spectra are distinguishable and shows a wider Stokes shift as the concentration of perylene increases. The fluorescence spectra containing $10^{-3}$ mole perylene has maximum emission at 472 nm while the fluorescence spectrum of $10^{-2}$ mole perylene is more intense and has maximum emission at 500 nm. At higher concentration of perylene i.e. at concentration $10^{-1}$ mole, the spectrum is completely structureless and the maximum emission occur at the wavelength 558 nm.

Fluorescence spectra of ternary naphthalene containing $10^{-1}$ mole pyrene and varying amounts of perylene are presented in Fig. 3.11. At the higher concentration of both impurities the spectra of naphthalene luminophors shows well defined and distinguishable structureless bands. The emission bands of naphthalene host are not observed in the spectra of any of the ternary luminophors. The emission region seems to be shifted towards red as concentration of perylene increases from $10^{-3}$ to $10^{-1}$ mole. The observed $\lambda_{\text{max}}$ are 501, 507 and 514 nm for corresponding concentrations $10^{-3}$, $10^{-2}$ and $10^{-1}$ mole perylene respectively. The well known excimer emission of perylene bulk crystal expected to occur at 630 nm, is not observed in any of the fluorescence spectra of ternary naphthalene system.113
Fluorescence mechanism:

In organic crystals, the absorption and emission do not always coincide. Similarly the spectra do not show emissions corresponding to the free molecules as in solution. Pure crystal luminescence originates from an electronic level of the crystal. The crystal luminescence involves the spontaneous transformation of excitons into photon. All other luminescent properties of the crystal involve the excitons only indirectly and the transformation to a photon occurs after the excitons have first decay into another excited level. Thus the impurities present in the pure crystal may give rise to the emitting sites having the energies lower than the energy of emitting level of the pure crystal. The trapping of excitons at these emitting levels may result in the emission from the crystal, which contain the impurities.

The naphthalene-pyrene bicomponent system is characterized by excimer emission of the pyrene. However, the addition of perylene as second impurity has given the emission towards longer wavelength side, and the emission regions are observed to depend upon the concentration of perylene. It is therefore believed that the perylene has the energetic interactions with the naphthalene or pyrene excitons. Earlier experiments have shown that the naphthalene and perylene has
no energetic interactions where as the perylene undergoes interaction with pyrene molecule. In pyrene-perylene crystalline bicomponent system the emission is arising at wavelength 499 nm due to exciplex formation between them. However, in naphthalene matrix, pyrene and perylene interactions have given the emissions at different wavelength, which are other than the exciplex emissions. It is hoped that the perylene and pyrene interactions introduce some metastable energy states, which are lying below the emitting level of the naphthalene crystals.

The naphthalene ternary system upon excitation by UV, produces singlet excited naphthalene excitons. The absence of naphthalene monomer emission in the fluorescence spectra of ternary naphthalene luminophors, represented in the Fig. 3.9-3.11 indicates that the naphthalene excitons are undergoing energy transfer process to pyrene molecule. The singlet excited energy level of the pyrene molecule is lying just below the corresponding energy level of the naphthalene. The singlet-singlet energy transfer is readily occurring and leads to a rapid migration of excitation energy through out the crystal lattice due to dipole-dipole interactions. This migration is known as exciton migration, which results in the formation of pyrene excitons. In addition to that the spectra, shown in the Fig. 3.9-3.11, do not
show monomer as well as excimer emission of pyrene, which is expected to occur in the region 380-410 and 450-490 nm respectively.\textsuperscript{114} It is therefore concluded that the excitation energy of pyrene exciton is trapped by the perylene molecule, by which the exciton energy is propagated over sufficiently large distance in the molecular crystal. Hence, the emitting level is possibly an associated electronic level produced by specific interactions between pyrene and perylene in the naphthalene host matrix. The pyrene and perylene molecules are having the similar lattice structure which involve the large lateral overlapping of $\pi$ molecular orbitals and the molecules exists in group of pairs when the ternary naphthalene mixed crystals were grown from the melt. The ternary systems of molecular solids are known to exhibit intermolecular $\pi$ orbital overlapping between the components and numerous van der Waal's interactions.\textsuperscript{115} As the fluorescence band represents the unusual characteristics, it is believed that emission must be arising from a CT state produced by the molecules grouped in pairs. Such states in molecular crystals are expected to lie above the lowest $\pi-\pi$ transitions but the geometry of the pairwise molecule may change during the excited state and there by lower the fluorescence level below the other states in the crystals.\textsuperscript{58} This change in geometry is due to a closer approach
of the two molecules in each pair. In pyrene and perylene the pair formation is more probable as these molecules have strong \( \chi \) -orbital overlapping.\(^6^4\) Such charge transfer band would lack in vibrational structure and as per expectation, the emission bands are broad and structureless. The different CT states, which are expected to produce by interaction of perylene and pyrene in naphthalene host matrix, are shown in the Fig.3.12. Matsui A. H. have reported the possibility of formation of such states in molecular crystals.\(^1^1^6\)

The origin of fluorescence in naphthalene ternary system due to formation of CT states is further confirmed by recording the excitation spectra of pure naphthalene and naphthalene doped by pyrene and perylene. Fig. 3.13 shows the excitation spectrum of bare and doped naphthalene. The excitation spectrum of bare naphthalene is sharp and structured. However, the presence of pyrene and perylene modifies the excitation spectrum of naphthalene. The excitation spectra of naphthalene containing pyrene and perylene are broad and structureless. The appearance of these structureless bands confirm the possibility of the formation of the metastable states in naphthalene ternary systems in the excited state.\(^1^1^7\)
Naphthalene doped by $10^{-3}$ mole pyrene and a) $10^{-3}$ b) $10^{-3}$ c) $10^{-3}$ mole perylene

Fig. 12. Charge transfer state in Naphthalene ternary systems containing pyrene and perylene.
Fig. 3.13
Excitation spectrum:

a. Pure naphthalene ($\lambda_{em} \text{ 395 nm}$) and
b. Naphthalene containing $10^{-2}$ mole pyrene with varying amounts of perylene
1. $10^{-3}$ mole perylene ($\lambda_{em} \text{ 472 nm}$)
2. $10^{-2}$ mole perylene ($\lambda_{em} \text{ 500 nm}$)
3. $10^{-1}$ mole perylene ($\lambda_{em} \text{ 561 nm}$)
3.4 Tricomponent naphthalene luminophors:

**Anthracene and pyrene doped naphthalene**

It is observed that the anthracene interacts energetically with naphthalene and acts to trap the excitation energy of naphthalene exciton. The result of this process is formation of anthracene exciton, which is exhibiting its characteristic fluorescence. In this binary naphthalene system, the use of another impurity may enhance the fluorescence or shifts the fluorescence of the system due to interaction with anthracene. Hence, the tricomponent system of naphthalene containing anthracene and pyrene were studied systematically.

**3.4.1 Naphthalene-anthracene binary system:**

Fig. 3.14 shows the fluorescenc spectrum of anthracene doped naphthalene (b). The fluorescence spectrum is structured and corresponds with the spectrum of the crystalline anthracene. The emission bands of naphthalene are quenched and the quenching is found to depend upon the concentration of anthracene. For the purpose of comparison the emission spectrum of pure naphthalene (a) and that of pure anthracene (c) recorded under identical experimental conditions are also shown in the same figure. In doped naphthalene the emission band peaking at 421 nm is due to $0 \rightarrow 0$ transition, and the emission bands corresponding to that of pure naphthalene are
Fluorescence spectra:

a. Pure naphthalene  

b. 10^{-2} mole anthracene doped naphthalene  

c. Pure anthracene

\[ \lambda_{ex} 316 \text{ nm} \]
partially quenched. The spectrum of mixed crystal also shows a shoulder in the region 440-475 nm due to some weak transitions occurring during de-activation of excited molecules. Thus, the careful examination of the figure 3.14, indicates that the fluorescence of naphthalene is quenched by the anthracene impurity. It is, therefore, concluded that the emissions arising from doped naphthalene crystal are due to anthracene impurity only.

It is worthwhile to note the following characteristic features of anthracene doped naphthalene system.

1) The intensity of anthracene doped naphthalene luminophor is greater than the intensity of bare anthracene.

2) The wavelength of maximum emission for anthracene doped naphthalene and bare anthracene is approximately the same ($\lambda_{\text{max}}$ = 421 nm).

3) The intensity of $0 \rightarrow 0$ band is more as compared to other weak bands appeared at the wavelengths 446, 474 nm. This observation indicate that the excitation energy of naphthalene exciton is transferred to anthracene impurity which produces excitation in $0 \rightarrow 0$ transitions.

4) The fluorescence spectrum of mixed crystal does not show characteristic emission of pure naphthalene.
Fluorescence mechanism:

From above observations following mechanism is proposed to explain the origin of fluorescence in anthracene doped naphthalene crystals.

The bicomponent system containing $10^{-2}$ mole of anthracene per mole naphthalene, when excited by radiation of wavelength 316 nm, singlet excited naphthalene excitons are produced, because the energy of excitation source corresponds to the excitaiton energy of naphthalene. The absence of naphthalene spectrum clearly indicates that naphthalene excitons while migrating through the mixed crystal lattice must be transferring its energy to the anthracene impurity. Such type of EET process in mixed stack crystals were reported at the lower temperature. The energy transfer mechanism can be better explained with the help of energy level diagram depicted in Fig. 3.15. The figure shows that the singlet and triplet energy levels of naphthalene are higher in energy than the corresponding energy levels of anthracene. Hence, the transfer of excitation energy from naphthalene singlet to anthracene singlet is more efficient. In the Fig. 3.14, $0 \rightarrow 0$ emission band of anthracene is enhanced, therefore, the excitation must occur in the $0 \rightarrow 0$ transition in anthracene by
Fig. 3.15 Energy level diagram of naphthalene, anthracene and pyrene.
In order to confirm EET process, the effect of concentration of anthracene on the fluorescence of naphthalene mixed crystals have been studied. Fig. 3.16 shows the fluorescence spectra of naphthalene containing different amounts of anthracene. From the figure it is noted that, as the concentration of anthracene increases intensity of the emission band at 412 nm increases without any change in spectral energy distribution. The addition of $10^{-3}$ mole of anthracene partially quenches the emission of naphthalene. The short wave emission band of naphthalene appears in the region 325-375 nm and a prominent structured emission of anthracene appears in the region 400-500 nm. The intensity of emission band corresponding to $0 \rightarrow 0$ transition is 838 a.u. at a wavelength 421 nm. When the concentration of anthracene is increased to $10^{-2}$ mole a considerable enhancement of $0 \rightarrow 0$ band is observed whose intensity is 997 a.u. as noted from the figure. The increase in concentration has not modified the shape of the spectrum of doped naphthalene. At the higher concentration enhancement effect was found to be slowed down. At a concentration of $10^{-1}$ mole of anthracene the intensity of the $0 \rightarrow 0$ band gets saturated at 1000 a.u. The rate of increase in
Fig. 3-16 Fluorescence spectra of anthracene doped napthalene

λ<sub>ex</sub> 316 nm

- --- 10<sup>-3</sup> mole anthracene
- --- 10<sup>-2</sup> mole anthracene
- --- 10<sup>-1</sup> mole anthracene
intensity of the system is more in the concentration range $10^{-3}$ to $10^{-2}$ mole anthracene. However, the observed decrease in the rate of fluorescence enhancement in the range $10^{-2}$ to $10^{-1}$ mole impurity concentration is due to the concentration quenching effect. At the higher concentrations, the rate of formation of anthracene excitons by EET process between naphthalene and anthracene is decreased and the rate of non-radiative transfer of energy between anthracene excitons and ground state anthracene molecule is increased.

3.4.2 Naphthalene-anthracene-pyrene ternary system:

The highly fluorescent systems of naphthalene emitting with blue fluorescence could be used for their utility in electronic industry for the production of fluorescent lamps and similar type of solid state devices, if their intensity is enhanced further. The pyrene is known to sensitize the fluorescence of anthracene\textsuperscript{26}. Therefore, the use of pyrene as second impurity may act to enhance the fluorescence of naphthalene-anthracene system. Fig.3.17 shows the fluorescence spectrum of naphthalene containing $10^{-2}$ mole of anthracene (a) and fluorescence spectrum of naphthalene containing $10^{-2}$ mole of anthracene (b) and $10^{-3}$ mole of pyrene (c). The addition of pyrene does not modify the nature and shape of the spectrum. However, it is worthwhile to note that the fluorescence intensity
Figure 1: Fluorescence spectra of naphthalene containing

a) $10^{-2}$ mole anthracene

b) $10^{-2}$ mole anthracene and $10^{-3}$ mole pyrene
of $0 \rightarrow 0$ emission band is considerably increased by addition of pyrene. The spectrum of naphthalene containing $10^{-2}$ mole anthracene shown in Fig. 3.17(a) was recorded under medium sensitivity of the spectrofluorometer and has intensity 997 a.u. The fluorescence spectra of the naphthalene containing $10^{-2}$ mole anthracene and $10^{-3}$ mole pyrene recorded under the medium sensitivity saturates and emission band gets flattened as shown in the Fig. 3.17(b). Therefore, the emission spectra of all ternary 'naphthalene systems were recorded under low sensitivity of the instrument.

Fig. 3.18 represents the fluorescence spectra of naphthalene ternary system containing $10^{-2}$ mole anthracene and varying amounts of pyrene. The examination of the spectra shown in the figure reveals that the emission of anthracene impurity gets enhanced and enhancement effect depends on the concentration of pyrene. The monomer and well known excimer fluorescence$^{121}$ of pyrene are not observed in the region of spectrum studied. We could not detect the fluorescence at very high concentration of pyrene and anthracene. The fluorescence intensity of naphthalene ternary system found to depend linearly with the concentration of pyrene added as a second impurity.
Fluorescence spectra of naphthalene containing $10^{-2}$ mole anthracene and
a) $10^{-3}$ mole pyrene
b) $10^{-2}$ mole pyrene
c) $10^{-1}$ mole pyrene
**Mechanism for fluorescence enhancement:**

An attempt has been made to understand the increase in intensity of fluorescence by pyrene. In the anthracene-tetracene system, blue emission of anthracene is strongly quenched. Our experimental results are in contrast with this system, as we could not detect emission from pyrene. We propose an alternative mechanism to explain the observed enhancement effect.

The absorption spectra of thin film of the naphthalene ternary systems are shown in Fig. 3.19. The spectrum is structured and the absorption bands are identical with those observed in absorption spectra of pure naphthalene. The absorption bands of crystalline pyrene and anthracene are not observed in the spectral range of absorption wavelengths. From the absorption study it is concluded that in naphthalene ternary system, only naphthalene is absorbing energy from excitation source, whereas, anthracene and pyrene are not involved in the primary absorption process.

The excitation of the naphthalene ternary system by radiation of wavelength, 316 nm produces singlet excited naphthalene excitons, as explained earlier in the naphthalene-anthracene system. The energy of naphthalene exciton is trapped by anthracene and anthracene excitons are produced.
Fig 3.19: Absorption spectra of pure naphthalene (a) and naphthalene ternary system (b) in thin film.
The energy of anthracene excitons is not trapped by pyrene because the fluorescence spectra of naphthalene ternary systems, does not show the emission of pyrene. In addition, the singlet energy level of pyrene is lying above the corresponding level of anthracene. Therefore, the transfer of energy from anthracene exciton to pyrene is improbable. However, the singlet energy level of pyrene, lie just below the corresponding singlet of naphthalene. As per our earlier observations, the pyrene is found to accept the excitation energy from naphthalene to produce its singlet excitons. From these observations, it is believed that, in the naphthalene ternary system both, anthracene and pyrene are trapping the excitation energy of naphthalene excitons. The probable photophysical process is shown in the energy level diagram depicted in Fig. 3.15. The energy level diagram is constructed on the basis of information available in the literature. Figure shows the absorption of the energy by the naphthalene which is followed by vibrational relaxation and resulted in the formation of thermally relaxed singlet excited naphthalene. The probable EET processes occurring between naphthalene-anthracene and naphthalene-pyrene are indicated in the figure. The absence of emission of pyrene led us to assume that the pyrene excitons are not deactivating radiatively. Therefore, it is assumed that
the triplet states of pyrene and anthracene must be populated by intersystem crossing as shown in the figure. The process is intermolecular and produces triplet excitons of anthracene and pyrene. The formation of triplet excitons leads into the triplet-triplet annihilation to produce singlet excited anthracene molecules.\textsuperscript{122}

\[ A^{*T1} + P^{*T1} \rightarrow A^{*S1} + P_{S0} \]

The triplet-triplet annihilation results into population of \( S_1 \) states of anthracene and increases the intensity of anthracene fluorescence in the presence of pyrene impurity. Quenching of anthracene emission at very high concentration of pyrene may be due to optical detrapping.